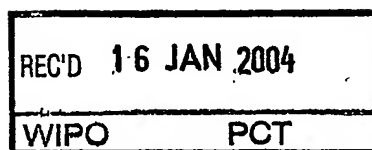


PCT/NZ03/00289



## CERTIFICATE

This certificate is issued in support of an application for Patent registration in a country outside New Zealand pursuant to the Patents Act 1953 and the Regulations thereunder.

I hereby certify that annexed is a true copy of the Provisional Specification as filed on 6 January 2003 with an application for Letters Patent number 523468 made by Auckland UniServices Limited.

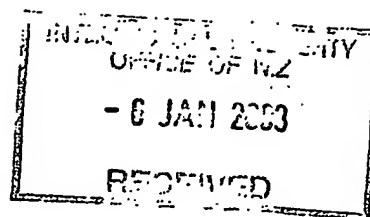
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*Neville Harris*

Neville Harris  
Commissioner of Patents, Trade Marks and Designs





*Patents Form No. 4*

# **Patents Act 1953**

## **PROVISIONAL SPECIFICATION**

### ***Electrochemical process and apparatus***

We, Auckland UniServices Limited, of Level 9, 70 Symonds St., Auckland 1000,

do hereby declare this invention to be described in the following statement:

## *Electrochemical process and apparatus*

### Introduction to the Invention

This invention relates to the electro-chemical process of electrolysis and in particular to a process and apparatus for applying electrolysis for the in-situ polishing, cleaning and/or sterilisation of metallic surfaces.

### Background of the Invention

Electrolysis is the chemical decomposition of substances, or electrolytes, by an electric current passed through the substance in a dissolved or molten state. The substances are ionized into electrically charged ions, and when an electric current is passed through them by means of conducting electrodes, the ions move towards the oppositely charged electrodes thereby giving up their electric charges to become uncharged atoms or groups, and are either liberated or deposited at the electrode or react chemically therewith.

Electrolysis has wide ranging industrial applications and is primarily used as a method of deposition at the cathode or sacrificial degradation at the anode. Electrolysis also finds application in cleaning and polishing techniques but, to date, has not been fully explored to its potential. The food industry and, in particular, the dairy industry suffers from particular problems associated with cleaning production machinery including heat exchangers. To date, machinery involved in the handling of milk and other dairy products must be shut down entirely for an extended period of time during cleaning operations. The cleaning involves flushing large amounts of caustic cleaning agents through the machines in order to remove residues build up and contamination. Acid cleaning may also be required some times. Once the cleaning is finished the machine must then be rinsed very thoroughly to remove all traces of these cleaning elements and reassembled and recommissioned. These cleaning problems are particularly associated with the cleaning and maintenance of heat exchangers, but extend to other componentry and also to other industries.

### Statement of Invention

In one aspect the invention provides a method of applying an electrochemical influence to a component of a machine having a metallic surface in need of cleaning, polishing and/or sterilisation; said method

comprising making said component part of an electrolytic system including the steps of:

- 5 a) applying an electrolyte solution to said component in situ; and
- b) applying a voltage between said component and said electrolyte.

The component may act as a cathode in said system, or may act as an anode, or may separately act as cathode and anode. In the latter case, a switching device may cause the component to switch between acting as an anode and a cathode during operation.

In another aspect the invention provides an in-situ method for polishing a bank of metallic surfaces said method comprising making said metallic surfaces part of an electrolytic system including the steps of:

- 15 a) applying an electrolyte solution to said metallic surfaces in situ;
- b) applying a voltage between adjacent metallic surfaces which act respectively as cathodes and anodes; and
- c) circulating said electrolyte about said metallic surfaces.

20 The metallic surfaces may be defined by plates of a heat exchanger.

In another aspect the invention provides a method of cleaning fouled metal surfaces said method including the steps of:

- 25 a) applying an electrolyte solution to said metal surface in situ; and
- b) applying a voltage to said metal surfaces and said electrolyte.

The voltage may be applied to said metal surface causing same to act as either anode or cathode. Instead a switching device may periodically cause the metal surface to switch between acting as an anode and as a cathode.

The electrolyte may be selected from phosphoric acid or sodium hydroxide.

In another aspect the invention provides a method of sterilising a component of a machine having a metal surface said method including the steps of:

- a) applying an electrolyte solution to said component in situ; and
- b) applying a voltage to said metal surface and said electrolyte.

5 The method may include the step of applying said voltage to said component with the component acting as either anode or cathode. Instead a switching device may periodically cause the component to switch between acting as an anode and as a cathode.

The voltage applied may be varied in a suitable manner so as to limit the current applied during electrolysis.

10 In another aspect the invention provides an electrochemical apparatus comprising an electrolyte to be applied to in-situ metallic components of a machine requiring treatment according to any of the previously described methods and a voltage control means for applying a voltage to said electrolyte with said metallic components acting as either anode or cathode.

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#### Brief Description of the Drawings

The invention is now described by way of example with reference to the accompanying drawings in which

20 Figure 1 shows a schematic block diagram of electrochemical apparatus, in accordance with the invention, as used in Example 1 below;

Figure 2 shows an electrolytic cell for simulating treatment of a metal component to be treated as described in Example 1 below;

Figure 3 shows a schematic block diagram of electrochemical apparatus, in accordance with the invention as used in Example 4 below;

25 Figure 4 shows a test component for Example 4 below as used in the apparatus of Figure 3;

Figure 5 shows a cleaning profile for Example 4;

Figure 6 shows a further cleaning profile for Example 4; and

Figure 7 shows a yet a further cleaning profile for Example 4.

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### Detailed Description of the Invention

#### **Example 1: In-situ Polishing of Heat Exchangers**

5 In Figure 1 of the drawings, reference numeral 10 generally designates a first example of electrochemical apparatus, in accordance with the invention, for treating metal components. The apparatus 10 includes an electrolyte tank 12 which supplies an electrolyte to a metal component 14, illustrated as plates of a heat exchanger. The electrolyte is pumped to the component 14 by a  
10 pump 16 through a control valve 18. The current in the circuit of the apparatus is maintained constant by a variable voltage controller 20.

The metal component or part 14 to be electropolished is placed in contact with a phosphoric acid base electrolyte and is subjected to direct current. The current is applied by way of the variable voltage controller 20 to  
15 maintain the magnitude of the applied current constant as resistance varies during the electrochemical treatment. The metal part 14 is made anionic (+) in the electrochemical system. For some types of plate heat exchangers, in which each heating plate is not electrically in contact with an adjacent plate, electropolishing can be applied in-situ by using the adjacent pair of heating  
20 plates as anode and cathode respectively. In order to achieve maximum efficiency the electrolyte is pumped through the heat exchanger continuously.

Experimental conditions: 5% (w/w) phosphoric acid as electrolyte, 5-10 V/cm electric field strength, 15-30 minutes treating time.

In high concentrations of phosphoric acid electrolyte (>55%), the removal  
25 rate of stainless steel is about 127 microns in 1.64 amp-minutes per square centimetre.

The electropolished plate surface shows a different lustre (or light tone) when compared to the unpolished surface. In order to obtain some microscopic details of electropolishing effects to the stainless steel surface, a  
30 group of auxiliary experiments were conducted on small stainless steel plates by using the electrolytic cell as shown in Figure 2.

Polishing tests for a microscopic investigation were carried out under the same voltage-current conditions using smaller pieces in the specially constructed cell as follows:

35

Samples: 2.5 cm x 9 cm x 0.12 cm stainless steel pieces.

Pre-treatment: scored with sandpaper to make directional lines on the work piece.

Electrolyte solution: 1) phosphoric acid 5%, sulfuric acid 5% and water. 2) phosphoric acid 30%, sucrose 40% and water.

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The in-situ heat exchanger plates demonstrated a polished effect. All the advantages of conventional electrochemical polishing for surface pre-treatment can be expected to be preserved during in-situ polishing processes. Some typical advantages are:

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- Removes oxides
- Passivates the stainless steel surfaces
- Hygienically cleans the treated surfaces
- Decarbonises the metal surfaces
- 15 - No hydrogen embrittlement after sufficient treatment
- No directional lines after sufficient treatment
- Smooths surface and reduces friction

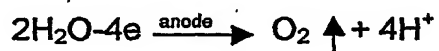
Such in-situ processing can be optimized to achieve equipment specific purposes.

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### Example 2: Enhanced Cleaning of Fouled Metal Surfaces

When an electric field is applied to a fouled metal surface, besides electropolishing, it can also remove the fouling. Gas bubbles are formed as a result of electrolysis of the solution on the surface of the electrodes.

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The electrochemical reactions give the following results:

- The vicinity of the anode surface became more acidic because of the formation of protons ( $\text{H}^+$ ). This causes removal of mineral deposits.

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- The vicinity of the cathode surface becomes more alkaline because of the formation of hydroxyls ( $\text{OH}^-$ ). This causes swelling of protein deposits making it easier to remove them.
- 5 - The gas bubbles formed provide an additional physical force to dislodge the attached foulant, whether mineral or protein.

#### **Fouling removal in phosphoric acid**

10 The electrolyte used was phosphoric acid used of 5% (w/w). The foulants were prepared by boiling milk. Stainless steel specimens were placed on a heated bottom of a beaker for at least two hours to allow the development of milk fouling formed by thermal denatured protein.

The fouled stainless steel specimen was mounted in an electrolytic cell as one of the electrodes. The gap between anode and cathode was set at 15 about 6mm. The initial voltage applied was 5 V (DC) allowing an 8.3 V/cm electric-field strength and 0.2 A/cm<sup>2</sup> current density for electrolysis. When the electric field was applied, large amounts of gas bubbles were formed on the electrode surface which provided a physical force to assist in dislodging the attached foulant. As a comparison, one of the sample specimens was soaked 20 in the same phosphoric acid solution for 24 hours. It was found that manual brushing had to be used to obtain the same cleaning result.

Electrolysis appears to be so effective in removing fouling that even some burnt-hardened crust on metal surfaces can be removed. The samples were prepared by heating the stainless steel specimens to about 300-350°C, 25 and then putting several drops of milk onto them resulting in the milk deposits drying out and becoming burned eventually to form a hardened skin.

#### **Fouling removal in NaOH solution**

It has also been found that it was even more effective to remove milk 30 fouling using an NaOH dilute solution (0.5 wt %; which is the recommended optimal concentration for milk foulant removal) as an electrolyte and electrolysis at a similar strength as above. In tests without electrolysis, the foulant swelled after being in contact with the NaOH solution. Because of the lack of fluid shear, the deposit would stay swollen but would not come off the 35 metal surface after more than half an hour. When the specimen was subjected to electrolysis after the similar foulant was put in contact with the solution,



swelling of the foulant started almost immediately and some 10 to 15 min thereafter, the foulant was removed and a clean metal surface emerged.

### **Example 3: Sterilisation of Microbial Contaminated Metal Surfaces**

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When an electric field is applied to a fouled metal surface sterilisation is evidenced.

The experimental conditions were:

- 10 4 stainless steel slices (2 cm x 10 cm);
- 15wt% whole milk as the "culture" liquid for putting live bacteria onto the metal surfaces;
- agar gel as the growth medium for live cell counts;
- 0.5% phosphate acid (pH 1.8);
- 15 Current density:  $0.2 \text{ A/cm}^2$ ;
- Field strength:  $8 \text{ V/cm}$ .

The procedures for the microbial tests were:

- 20 (1) Weigh out 120 g whole milk powder into 800ml water in a beaker, heat and stir until milk powder is completely dissolved;
- (2) Immerse the steel slices into the milk and culture at  $37^\circ\text{C}$  overnight;
- (3) Prepare 20 sterilised plates with agar and 20 sterilised bottles with water, 4  
25 of them of 10 ml capacity, the other 16 of 9 ml capacity;
- (4) Electrolyse the steel slices in the 0.5% phosphate acid separately for 10 minutes and 20 minutes;
- 30 (5) Scrape the surface of the slices with cotton;
- (6) Wash the cotton in the bottle of 10 ml water;
- (7) Dilute the suspensions to 10, 100, 1000 and 10,000 times;
- 35 (8) Transfer 1.0 ml of each diluted suspension to each plate with agar;

(9) Culture the plates at 37°C for 2 days.

The results of the tests are given in the following table.

5

The results suggest that after electrolysing under the above electrifying strength, the live bacteria were deactivated effectively by the electrolysis actions.

10

Process	*10	*100	*1000	*10,000	*100,000
Electrolysing for 20 min	No	No	No	No	No
Electrolysing for 10 min	No	No	No	No	No
Immersed in electrolyte for 20 min	Not sure	No	No	No	No
Immersed in electrolyte for 10 min	Too many to be counted	Too many to be counted	About 100	8	No

**Example 4: Removal of protein-gel deposits from inner surface of a metal tube.**  
**Experimental apparatus**

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An experimental apparatus for the removal of protein-gel deposits from an inner surface of a metal tube is illustrated schematically in Figure 3 of the drawings and is designated by the reference numeral 30. The apparatus 30 consists of a stainless steel tube 32 (ID = 16 mm and length = 150 mm) which forms the test piece and which, as will be described below, has been pre-coated with a whey protein concentrate (WPC) gel film using a rotation rig.

A NaOH solution reservoir 34 contains heating coils 36 and an agitator 38. The reservoir 34 contains the NaOH cleaning solution of a given concentration and is maintained at the required temperature by the heating coils 36. The cleaning solution is circulated through the apparatus by a pump

40. Flow velocity of the cleaning solution in the apparatus 30 is controlled by a valve 42 and is monitored by a float type flow meter 44.

Downstream of the tube 32, the cleaning solution, containing the removed deposits, is continuously transported to a UV spectrophotometer 44 by a sampling pump 46. The spectrophotometer 44 is connected to a computer 48. Once the material has been sampled it is discharged through a drain 50.

The apparatus records ultraviolet (UV) light absorption at 248 and 256 nm at 10 second intervals to monitor the cleaning process.

### **The preparation of the tube 32**

10

A commercial WPC powder (80.4 wt.% protein, 7.4 wt.% carbohydrate, 5.6 wt.% fat, 3.8 wt.% moisture, 2.8 wt.% ash, pH 6.5) was purchased from a local dairy company. Aqueous dispersions of 25 wt.% WPC were prepared in a test beaker by agitating until a uniform suspension was obtained. The WPC solution was then accurately weighed and poured into a stainless steel sleeve 52 (Figure 4). Both sides of the sleeve 52 were tightly sealed by plugs (not shown). The sleeve 52 was placed on a rotating device and immersed in a water bath at a temperature of about 79.5 °C. The sleeve 52 was rotated while in a horizontal orientation for about 30 minutes at a rotational speed of about 60 rpm. The sleeve 52, coated with a WPC gel film 54 (Figure 3), was then cooled by running tap water over the outer surface of the sleeve 52. The coated sleeve 52 was inspected in order to ensure that it had a continuous uniform WPC gel film 54 before being put into the cleaning apparatus 30. The density of the WPC gel film 54 was about  $1.10 \pm 0.02 \text{ g.cm}^{-3}$ , which is similar to that of skim milk deposits ( $1.1\text{-}1.2 \text{ g/cm}^3$ ).

The plugs were removed from the sleeve 52 and a metal rod 56 was inserted into the sleeve 52 to act as an anode or cathode in the electrolysis process. PVC tubing 58 was applied to each end of the sleeve 52 to form the tube 32 to be mounted in the apparatus 30.

30

### **Protein concentration measurement**

The most frequently employed spectral range for protein analysis is between about 250 and 320 nm (the near ultraviolet region), UV absorbance

measurements in this region providing the most accurate result for determining protein concentrations. The sensitivity of this method is high enough to determine a very dilute protein solution (1mg/L) encountered in the cleaning study. In this study it has been found that using 0.5 wt.% NaOH solutions instead of pH 13 buffer solutions did not adversely affect the UV absorbence. A linear relationship between the UV absorbence difference at 248 and 256 nm and the WPC concentration in the cleaning solution was established. Therefore, a continuous and non-invasive UV spectrophotometric method can be used to monitor the cleaning process on-line. The following expression is used for the estimation of protein concentration in the cleaning solutions:

$$WPC \text{ concentration (g/L)} = 1.0368(A_{248} - A_{256}) + 0.0005$$

where  $A_{248}$  and  $A_{256}$  are the values of UV absorbence at the wavelengths of 248 and 256 nm, respectively.

## Results

Figures 5-7 show the results of cleaning the tube 32 with the technique of the present invention bench-marked against conventional (or normal) cleaning without the applied electro-chemical influence. In each of Figures 5-7, the Y-axis (absorption difference) is the measure of the concentration of the removed materials in the exit-flow from the test section 32.

### 1. Cathodic cleaning

Figure 5 shows the effect of cathodic cleaning. The cleaning temperature was about 65°C, the flow velocity was about 0.24 m/s and the cleaning solution was about 0.5 wt% NaOH solution. The WPC gel film was about 0.6mm thick.

It is to be noted that, in comparison to normal cleaning without in-situ electrolysis, the WPC gel was removed from the tube 32 at a much higher rate.

Figure 6 also shows the application of cathodic cleaning in comparison to normal cleaning but at a lower current density. The remaining experimental parameters were the same as for the experiment shown in Figure 5. Once

again, using the technique of the present invention, even at the lower current density, resulted in a more efficient cleaning operation being effected.

## 2. Periodic polarity reversal electrocleaning

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Figure 7 of the drawings shows the result where the anodic and cathodic modes were switched about every 10 seconds with an applied voltage of about 3V and a current density of  $0.02\text{A}/\text{cm}^2$ . The flow rate of the NaOH solution was about 0.3 m/s, its temperature was about  $65^\circ\text{C}$  and its concentration was about 0.5 wt%. Once again the WPC gel film was about 0.6mm thick.

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It is to be noted therefore that, in all the cases illustrated in Figures 5-7, the electro-chemical method of the invention gives superior results compared with the conventional method.

The process and apparatus of the invention provides for in-situ polishing, cleaning and/or sterilisation of metallic components which can be treated in place without dismantling of machinery of which the components form part.

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The invention provides a method which can be widely applied to a range of industrial process systems enabling efficient maintenance to be accomplished without long down time for repairs.

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Thus, an advantage of the invention is to harness the principles of electrolysis to assist in the polishing, cleaning and/or sterilisation of metallic componentry. The invention uses the principles of electrolytic decomposition for the maintenance and upkeep of a wide range of industrial machinery where the electrolyte is applied in situ to the machine in question as a liquid flowing through the machinery components, without the machine requiring any degree of dismantling. The application of electrolyte to the intact machinery, utilizes a much lower level of electrolyte in suspension and allows maintenance and cleaning operations to be conducted in situ, resulting in a very low down time and the use of caustic and other cleaning agents at far lower concentrations.

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Accordingly, the invention provides for the first time, methods utilizing principles of electrolysis for cleaning, polishing, sterilizing and maintenance of complex industrial machinery without the need for dismantling or disassembling such machinery into its component parts for cleaning and maintenance. The combined use of mild caustic solutions to remove protein or mild acidic solutions to remove mineral deposits as appropriate, in conjunction with careful control of voltage to maintain the current constant, as appropriate, results in a

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highly efficient method as provided by the invention, allowing regular and speedy maintenance with minimal down time. The invention has particular application to the dairy industry, where fouled heat exchangers can be readily cleaned with minimal shut down time and minimal interruption to production. In  
5 such application involving electrolytic polishing, minimal interference and damage is caused to machinery components as the electrolytic action removes only minuscule amounts of the metal components. The method of the invention thereby serves to greatly extend the life of such components.

It will be appreciated by persons skilled in the art that numerous  
10 variations and/or modifications may be made to the invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

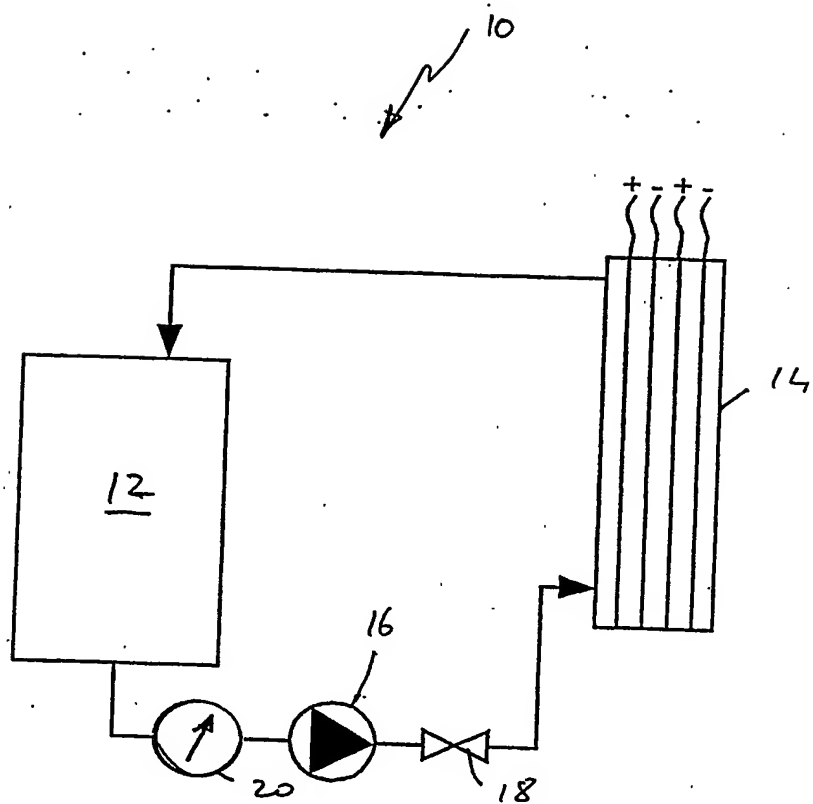


FIG. 1

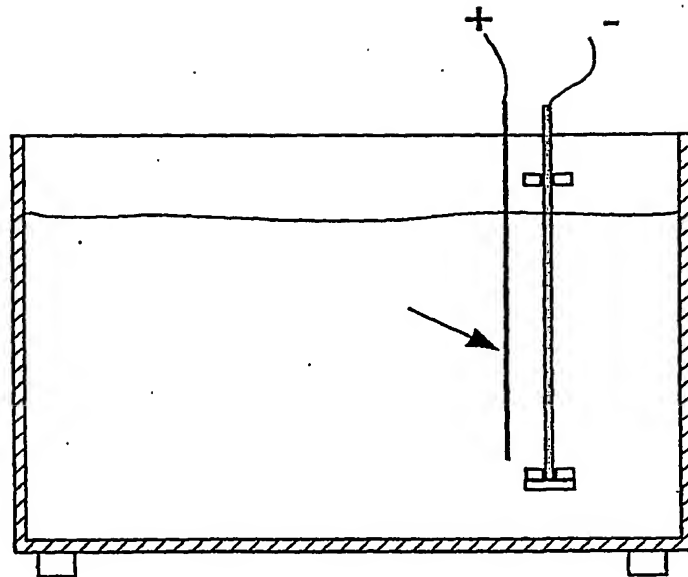


FIG. 2



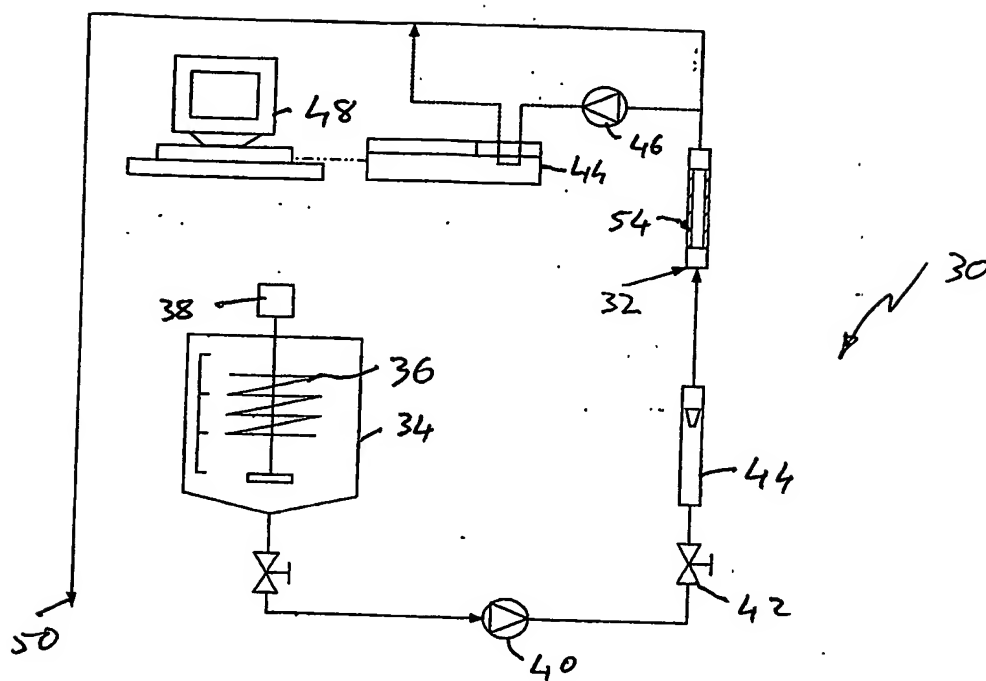


FIG. 3

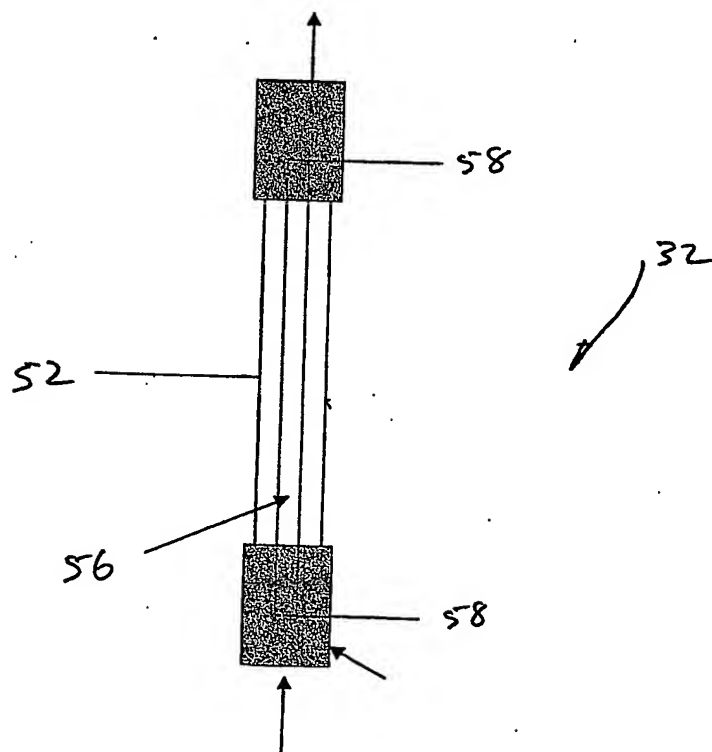


FIG. 4

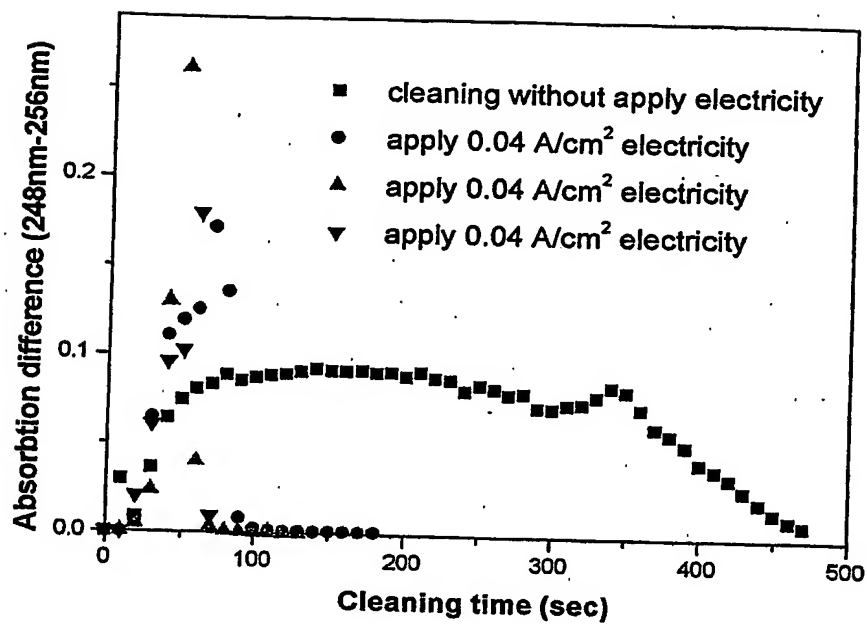


FIG. 5

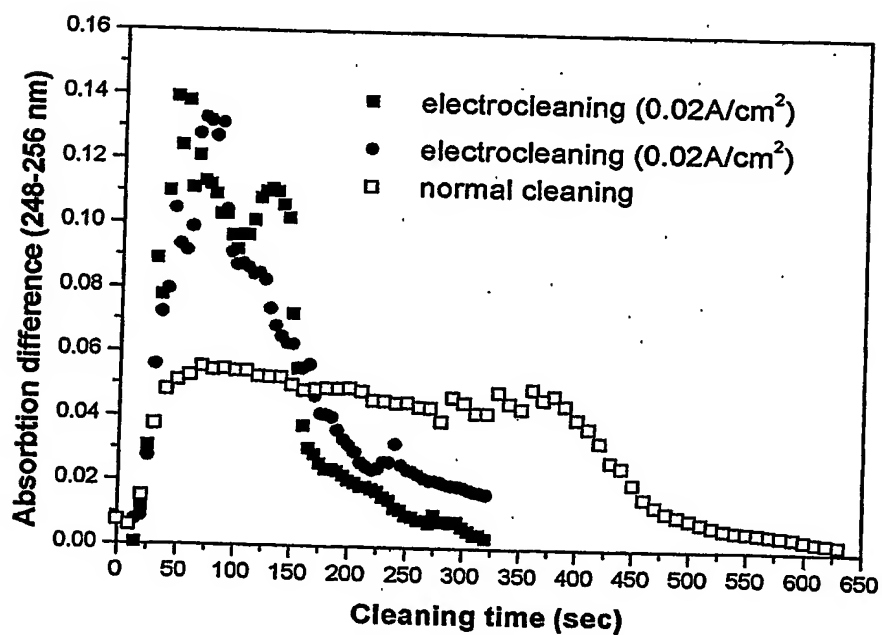


FIG. 6

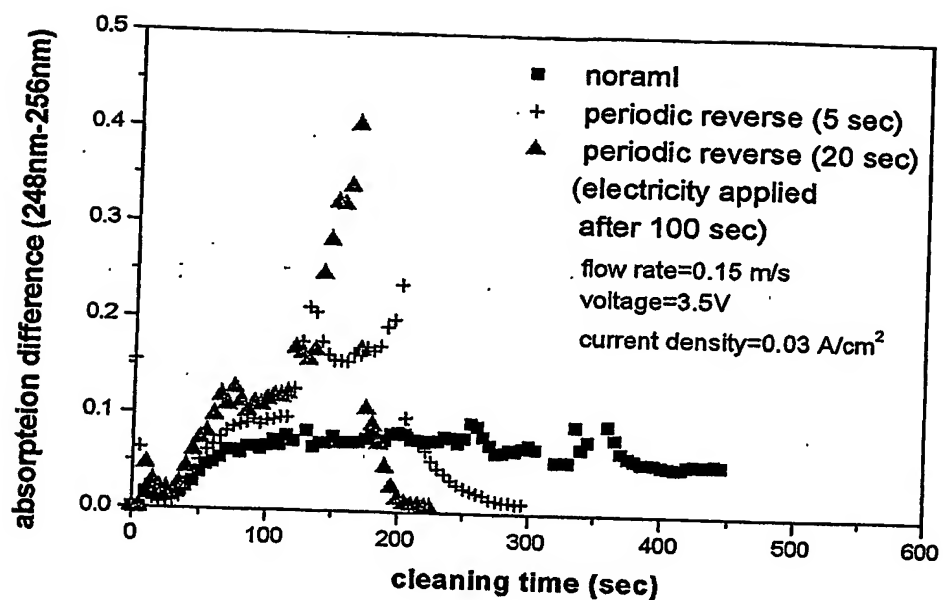


FIG. 7